

THE BAND SPECTRUM OF SILVER CHLORIDE

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ABSTRACT

Analysis of vibrational structure. —The electronic band system of AgCl extending from $\lambda 3124$ to $\lambda 3400$ has been obtained in emission and absorption, the latter under high dispersion. A complete vibrational quantum analysis has been carried out, giving the following formula for the heads of the bands of the molecule $\text{Ag}^{107}\text{Cl}^{36}$:

$$\nu = 31574.4 + 275.0\nu' - 6.20\nu'^2 - 0.133\nu'^3 - 342.4\nu'' + 1.163\nu''^2.$$

The data give $\omega_e'' = 343.6 \text{ cm}^{-1}$, $\omega_e' = 281.0$, and $\nu_e = 31606.9 \text{ cm}^{-1}$. Vibrational quantum numbers have been assigned to Franck and Kuhn's data for AgBr and AgI.

Isotope effects. —The vibrational isotope effect was observed for both the Cl and the Ag atoms. The complete spectrum consists of four overlapping systems due to the four possible isotopic molecules. The order of magnitude of the isotope shift for the Cl isotope effect was 1 to 30 cm^{-1} ; for the Ag isotope effect, 1 to 4 cm^{-1} . The agreement of observed shifts with those calculated from the equations recently derived by Birge (not yet published) is close.

Energies and products of dissociation. The heats of dissociation of the AgCl molecule are $D_0'' = 3.11$ volts in the normal state, $D_0' = 0.31$ volt in the excited state. The energy of excitation of the atoms resulting by dissociation from the excited state is 1.10 ± 0.12 volt. This value can be explained if it is assumed that $^2D'$ states exist in Ag as in Cu and Au. It is concluded that the silver halides dissociate from the excited state into a silver atom in a $^2D'$ state and a halogen atom in the metastable $^2P_{1/2}$ state.

INTRODUCTION

THE spectrum of silver chloride vapor consists of a system of single-headed bands in the ultra-violet, all the bands being shaded toward the red. These bands were first obtained by Franck and Kuhn¹ in absorption and fluorescence. Their work was concerned chiefly with a study of the type of molecular binding of the silver halides AgI, AgBr, and AgCl. Their results indicate that these molecules are of the "atom-molecule" type, in contrast to the alkali halide "ion-molecule" type. AgCl gave only a discontinuous band spectrum, whereas AgBr and AgI each showed a single continuous spectrum in addition to bands. The heats of dissociation of AgI and AgBr were calculated from the long wave-length limit of the continuous spectrum assuming that the product of dissociation from the excited state were a normal silver atom and an excited halogen atom. The heats of dissociation were also found independently by extrapolation of the fluorescence series. But for AgCl no direct calculation was possible by either method. The authors were not able to assign vibrational quantum numbers for any of these band systems. No mention was made of an isotope effect.

¹ Franck and Kuhn, *Zeits. f. Physik*, **43**, 164 (1927); **44**, 607 (1927).

In the present research, a complete vibrational quantum analysis of the AgCl band spectrum has been made. Accurate determinations of the heats of dissociation of the molecule in both the normal and the excited states lead to new conclusions as to the products of dissociation of the silver halides. In addition, the vibrational isotope effect of both atoms simultaneously has been obtained.² This is the first time the silver isotope effect has been obtained in spectra.

EMISSION SPECTRUM

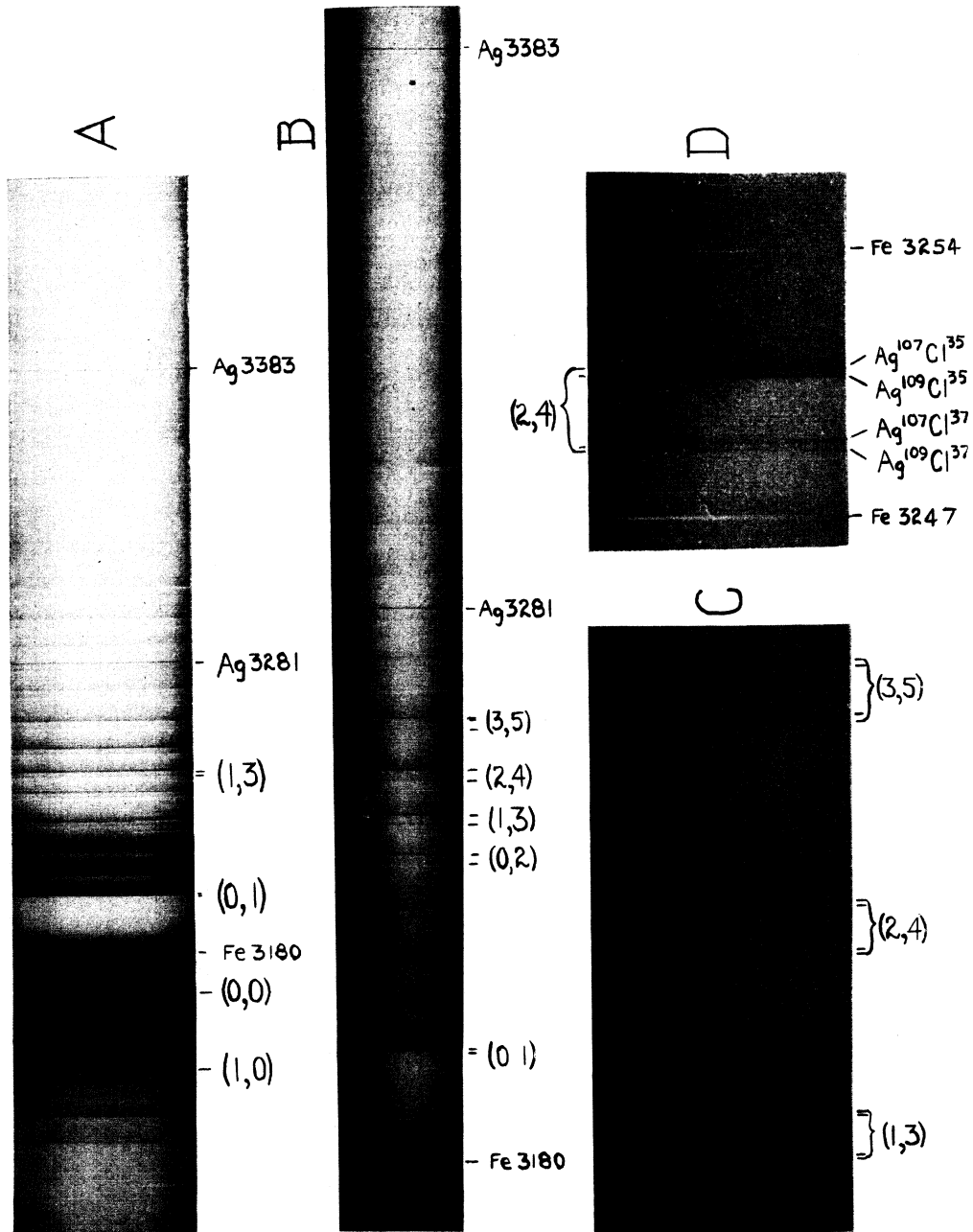
The silver chloride band spectrum was obtained in emission³ by viewing the region immediately above a long silver electrode covered with fused AgCl, in a high voltage discharge in hydrogen at about 1 mm pressure. Photographs were made with a quartz Hilger E2 spectrograph. The small number of bands appearing in emission permitted a ready assignment of vibrational quantum numbers. The heads of the following bands were obtained in emission: (0, 0), (1, 0), (0, 1), (1, 1), (2, 1), (1, 2), (3, 2), (2, 3), (3, 4). Of the bands recorded by Franck and Kuhn, those which do not fit into this assignment can be shown to belong to the fainter isotope molecule AgCl³⁷. In order to extend the observations of the isotope effect and to obtain accurate values for

TABLE I. Wave-lengths and wave-numbers of observed heads. F. & K., bands observed by Franck and Kuhn.

(v', v'')	Ag ¹⁰⁷ Cl ³⁵		Ag ¹⁰⁹ Cl ³⁵		Ag ¹⁰⁷ Cl ³⁷		Ag ¹⁰⁹ Cl ³⁷		F. & K.
	λ	ν	λ	ν	λ	ν	λ	ν	ν
(2, 0)	—	—	—	—	3114.60	32077.0	—	—	32096
(3, 1)	3124.17	31999.3	—	—	3124.79	31992.9	—	—	32005
(4, 2)	3135.10	31887.7	—	—	3135.39	31884.7	—	—	—
(1, 0)	3139.70	31841.0	—	—	3140.15	31836.4	—	—	31845
(2, 1)	3147.93	31757.7	—	—	—	—	—	—	31760
(3, 2)	3157.48	31661.7	—	—	—	—	—	—	31663
(0, 0)	3166.21	31574.4	—	—	—	—	—	—	31579
(1, 1)	3173.35	31503.4	—	—	3173.60	31500.9	—	—	31506
(2, 2)	3181.95	31418.2	—	—	3181.59	31421.8	—	—	31426 i
(0, 1)	3200.81	31233.1	—	—	3200.07	31240.3	—	—	31243 i
(1, 2)	3208.03	31162.8	—	—	3207.14	31171.4	—	—	31174 i
(2, 3)	3216.26	31083.0	—	—	3215.28	31092.5	3215.16	31093.7	31094 i
(3, 4)	3225.79	30991.2	—	—	3224.46	31004.0	—	—	30998
(0, 2)	3235.98	30893.7	3235.82	30895.2	3234.50	30907.8	3234.31	30909.6	30908 i
(1, 3)	3243.18	30825.0	3242.97	30827.0	3241.50	30841.0	3241.31	30842.8	30833
(2, 4)	3251.35	30747.6	3251.14	30749.6	3249.47	30765.4	3249.24	30767.6	30755
(3, 5)	3260.77	30658.8	3260.52	30661.2	3258.63	30678.9	3258.35	30681.5	30667, 30687
(4, 6)	3271.76	30555.8	3271.46	30558.6	3269.26	30579.2	3268.98	30581.8	30564
(1, 4)	3278.63	30491.8	3278.33	30494.6	3276.23	30514.1	3275.91	30517.1	30495
(2, 5)	3286.77	30416.3	3286.48	30418.9	3284.15	30440.5	3283.87	30443.1	30422
(3, 6)	3296.20	30329.3	3295.87	30332.3	3293.30	30356.0	3292.94	30359.3	30335, 30356
(4, 7)	3307.14	30228.9	3306.82	30231.8	3303.91	30258.5	3303.49	30262.3	30235, 30262
(2, 6)	3322.77	30086.7	3322.42	30089.9	—	—	—	—	—
(3, 7)	3332.14	30002.1	3331.73	30005.8	—	—	—	—	30008
(4, 8)	3343.11	29903.7	3342.70	29907.4	—	—	—	—	29912
(4, 9)	3379.55	29581.2	3379.10	29585.2	—	—	—	—	29590
(5, 7)	—	—	—	—	—	—	—	—	30443
(5, 8)	—	—	—	—	—	—	—	—	30118
(5, 9)	—	—	—	—	—	—	—	—	29795
(6, 10)	—	—	—	—	—	—	—	—	29655
(3, 8)	—	—	—	—	—	—	—	—	29689
(5, 10)	—	—	—	—	—	—	—	—	29475
(6, 11)	—	—	—	—	—	—	—	—	29327
(4, 10)	—	—	—	—	—	—	—	—	29270
(5, 11)	—	—	—	—	—	—	—	—	29161
(6, 12)	—	—	—	—	—	—	—	—	29014
(5, 12)	—	—	—	—	—	—	—	—	28839
(6, 13)	—	—	—	—	—	—	—	—	28694

² B. A. Brice, Phys. Rev. **34**, 1227 (1929) (Letter).

³ B. A. Brice, Phys. Rev. **33**, 1090 (1929) (Abstract).



SILVER CHLORIDE ABSORPTION

Fig. 1.

the heats of dissociation, it was considered worth while to photograph AgCl vapor in absorption under high dispersion.

ABSORPTION SPECTRUM

The absorption spectrum was obtained by passing white light from a tungsten quartz lamp through AgCl vapor. The salt was heated to about 900°C in an open quartz tube 2 ft long surrounded by an electric furnace. Photographs were taken using a 21 ft concave grating, giving a dispersion of 2.5 Å/mm in the first order and 1.3 Å/mm in the second order. The grating* is mounted according to Paschen in a temperature-controlled room. The photographs are reproduced in the accompanying plate. Photograph *A* shows the first order spectrum, *B* the second order; the enlargements *C* and *D* illustrate in more detail the isotope effect, showing the four heads composing each band. The comparison spectrum is that of an iron arc, the standard wave-lengths being taken from Kayser's Handbuch Vol. VII.

Table I gives the wave-lengths in air of the observed heads. The corresponding wave-numbers are corrected to vacuum by using Kayser's table. The values recorded are the mean of two independent measurements on a first order plate and one on a second order plate. The heads given by Franck and Kuhn are also recorded for comparison. It is evident that their measurements are from 3 to 10 cm⁻¹ too high.

VIBRATIONAL ANALYSIS

Throughout this paper the notation used will be as far as possible consistent with that proposed recently by Mulliken for the general theory of band spectra, and that proposed by Birge⁴ for the isotope theory. The *true* vibrational quantum number is integral, $v=0, 1, 2, \dots$; the *effective* quantum number is half-integral, $u=v+\frac{1}{2}$. Subscripts *e* refer to the vibrationless but impossible state for which $u=0$; subscripts 0 refer to the lowest possible vibrational state, for which $u=1/2$.

The possible energy levels of a non-rotating molecule are given by

$$G_u = \omega_e(u - x_e u^2 + y_e u^3 + \dots) \quad (1)$$

where ω_e is the mechanical vibration frequency for vanishingly small amplitude. The wave-numbers of the origins of the bands in the spectrum are

$$\nu = \nu_e + \omega_e'(u' - x_e' u'^2 + y_e' u'^3 + \dots) - \omega_e''(u'' - x_e'' u''^2 + y_e'' u''^3 + \dots) \quad (2)$$

where ν_e corresponds to the electronic energy change, and is defined as the origin of the band system. The classical vibration frequency is obtained from Eq. (1) by differentiation: $\omega_u = dG_u/du$. But experiment yields values of $\omega_{u+1/2}$, which is the spacing of the energy levels. From Eq. (1)

$$\omega_{u+1/2} = G_{u+1} - G_u = \omega_e u \left[1 - 2x_e(u + \frac{1}{2}) + 3y_e(u + \frac{1}{2})^2 + \dots \right] \quad (3)$$

* The Anderson grating used at present in this mounting is the property of Townsend Harris Hall, College of the City of New York.

⁴ R. T. Birge, unpublished work.

If the data are sufficient, a plot of the observed spacings $\omega_{u+1/2}$ against $u + \frac{1}{2}$ can be used to determine the constants of Eq. (2). The value of ω_u for any value of u can then be obtained from the resulting curve by interpolation or extrapolation. Eq. (2) will then represent the origins (or heads, in practice) of the observed bands.

It is found experimentally that for non-polar molecules the $\omega_u:u$ curve is linear for low values of u , and that extrapolation of the linear part to $u = u_0$ when $\omega_u = 0$ leads to a fairly reliable determination of the heat of dissociation.⁵ This gives $u_0 = \omega_e / 2x_e\omega_e$. Geometrically the heat of dissociation is given by the area under the $\omega_u:u$ curve:

$$D_e = \int_0^{u_0} \omega_u du = \frac{1}{2} \frac{\omega_e^2}{2x_e\omega_e} \quad D_0 = \int_{1/2}^{u_0} \omega_u du = \frac{1}{2} \frac{\omega_0^2}{2x_e\omega_e} \quad (5), (6)$$

Eq. (5) gives the heat of dissociation referred to the equilibrium state. Eq. (6) is the *true* heat of dissociation, referred to the lowest possible vibrational state. There will be a value D_0'' for dissociation by vibration from the normal state, and a value D_0' for the excited state.

Fig. 2 shows the observed heads of the most abundant molecule $\text{Ag}^{107}\text{Cl}^{35}$ arranged in the customary array which determines the true assignment of vibrational quantum numbers, and which yields the experimental values of $\omega_{u+1/2}''$ and $\omega_{u+1/2}'$. The intensity distribution here is characteristic of molecules having a small change in moment of inertia on electronic transition.

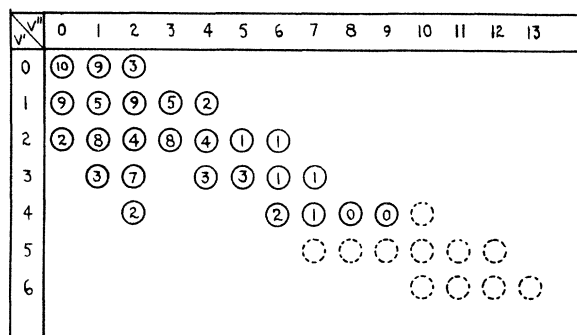


Fig. 2. Assignment of vibrational quantum numbers. Numerals indicate estimated intensities. Dotted circles are additional bands observed by Franck and Kuhn.

Table II contains the values of ω_u for corresponding u , including both the experimental, and the extrapolated and interpolated values, which are needed later for calculating the isotope shifts. In Fig. 3 the $\omega_u:u$ curves for the most abundant molecule are A'' , A' . The curve A' for the excited state is not a straight line.

⁵ Birge and Sponer, *Phys. Rev.* **28**, 259 (1926). See also *Bull. Natl. Res. Council*, No. 57 (1926), p. 131; R. T. Birge, *Trans. Far. Soc.* **25**, 707 (1929).

TABLE II. Values of ω_u .

u	$\text{Ag}^{107}\text{Cl}^{35}$		$\text{Ag}^{109}\text{Cl}^{35}$		$\text{Ag}^{107}\text{Cl}^{37}$		$\text{Ag}^{109}\text{Cl}^{37}$	
	ω_u''	ω_u'	ω_u''	ω_u'	ω_u''	ω_u'	ω_u''	ω_u'
0	343.6	281.0	342.4	—	336.0	276	—	—
$\frac{1}{2}$	342.4	275.0	341.3	275	334.9	270	—	—
1	341.3	268.3	—	—	—	263.6	—	—
$1\frac{1}{2}$	340.2	262	339.0	262	332.7	257	—	—
2	339.0	255.1	—	255.0	332.5	251.1	—	250.7
$2\frac{1}{2}$	337.8	249	336.8	249	330.5	245	—	—
3	336.5	242.8	—	242.4	329.9	238.5	—	238.4
$3\frac{1}{2}$	335.5	235	334.5	235	328.3	231.3	—	—
4	334.3	226.4	332.4	226.2	327.0	223.2	325.9	222.5
$4\frac{1}{2}$	333.2	217	332.2	217	326.2	214	—	—
5	331.9	206 ?	330.7	—	325.0	—	324.5	—
$5\frac{1}{2}$	330.8	194 ?	330.0	194	324.0	—	—	—
6	329.6	173 ?	328.9	—	322.9	—	322.2	—
$6\frac{1}{2}$	328.5	—	327.8	—	321.8	—	—	—
7	327.1	—	326.7	—	320.7	—	319.5	—
$7\frac{1}{2}$	326.2	—	325.6	—	319.6	—	—	—
8	325.2	—	324.4	—	—	—	—	—
$8\frac{1}{2}$	323.8	—	323.3	—	317.4	—	—	—
9	322.5	—	322.2	—	—	—	—	—
$9\frac{1}{2}$	321.5	—	—	—	—	—	—	—
$10\frac{1}{2}$	319.2	—	—	—	—	—	—	—
$11\frac{1}{2}$	316.8	—	—	—	—	—	—	—
$12\frac{1}{2}$	314.5	—	—	—	—	—	—	—

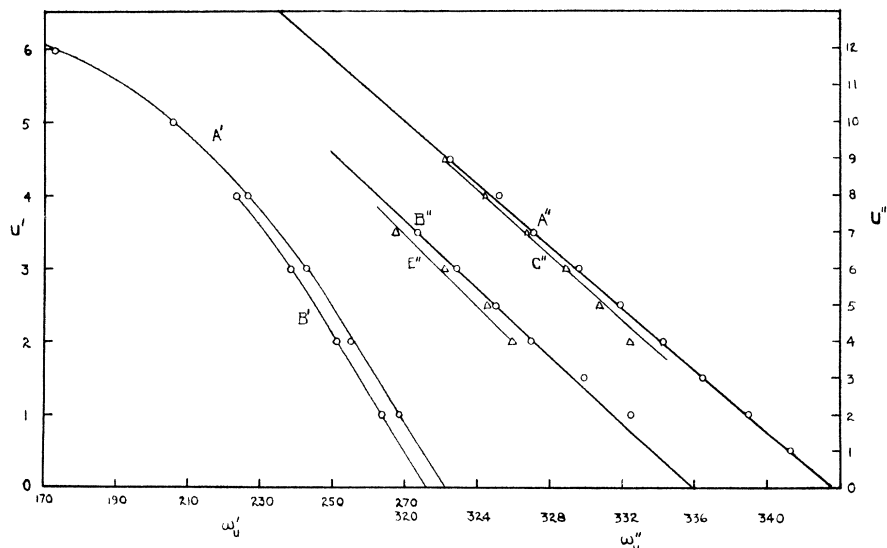


Fig. 3. ω_u : u curves: A'' normal, A' excited state of $\text{Ag}^{107}\text{Cl}^{35}$; B'' normal, B' excited state of $\text{Ag}^{107}\text{Cl}^{37}$; C'' normal state of $\text{Ag}^{109}\text{Cl}^{35}$; E'' normal state of $\text{Ag}^{109}\text{Cl}^{37}$.

The equation representing the heads of the bands for the molecule $\text{Ag}^{107}\text{Cl}^{35}$, from Eq. (2) and the above data is:

$$\nu = 31574.4 + 275.0\nu' - 6.20\nu'^2 - 0.133\nu'^3 - 342.4\nu'' + 1.163\nu''^2 \quad (7)$$

The value of u'' for which the spacings of the levels becomes zero is $u_0'' = 148$. By Eq. (5), $D_e'' = 25390 \text{ cm}^{-1} = 3.13$ volts; by Eq. (6), $D_0'' = 3.11$ volts. The latter is the true heat of dissociation of the molecule $\text{Ag}^{107}\text{Cl}^{35}$. Its accuracy is estimated as ± 0.10 volt. This agrees closely with the value 3.1 volts taken from thermochemical data.*

For the excited state, extrapolation of the $\omega_u : u$ curve is somewhat uncertain. It is safe to assume however that a maximum value will be set by extrapolating a straight line drawn through the first three points. This gives $D_0' = 0.33$ volt. A lower limit may be set by calculating the area under the actual curve, using the empirical equation. This gives 0.28 volt. Hence we may take $D_0' = 0.31 \pm 0.02$ volt.

THEORY OF THE ISOTOPE EFFECT

The theory of the vibrational isotope effect, first formulated by Mulliken,^{5a} has recently been applied in a form more convenient for calculation of isotope shifts in bands of high vibrational quantum numbers by Gibson,⁶ Patkowski and Curtis,⁷ and R. T. Birge.⁴ Professor Birge has given a thorough discussion of the applicability of this method, and has kindly made his results available to the writer in advance of their publication. In the following, his notation will be followed, and some of his equations given. Superscripts i will refer to the "isotope" or less abundant molecule, while letters without superscript will denote the "main" or more abundant molecule.

The vibrational energy of a non-rotating molecule as given by Mulliken^{5a} is $G_u = f(u\mu^{-1/2})$ where $\mu = M_1M_2/M_1 + M_2$, the effective or reduced mass of the molecule, M_1 and M_2 being the relative masses of the two atoms composing the molecule. If an isotope of one of the atoms is present, the reduced mass of the isotope molecule is μ^i , and if we let $\rho = (\mu/\mu^i)^{1/2}$ the vibrational energy of this molecule is $G_u^i = f(u\rho\mu^{-1/2})$. Hence for a given value of u , regardless of the functional form of G_u given by Eq. (1), we obtain G_u^i by replacing u by $u\rho$. Writing Eq. (1) for the isotope molecule:

$$G_u^i = \omega_e [u\rho - x_e\rho^2u^2 + y_e\rho^3u^3 + \dots] \quad (8)$$

Subtracting Eq. (1) from Eq. (8) we obtain the general form of the isotope shift, as given by Birge:

$$G_u^i - G_u = \omega_e [(\rho - 1)u - (\rho^2 - 1)x_eu^2 + (\rho^3 - 1)y_eu^3 + \dots] \quad (9)$$

When an electron transition occurs, this becomes, in terms of the wave numbers of the origins of the bands,

* Taken from ref. 1.

^{5a} R. S. Mulliken, Phys. Rev. **25**, 119 (1925).

⁶ G. E. Gibson, Zeits. f. Physik **50**, 692 (1928).

⁷ Patkowski and Curtis, Trans. Far. Soc. **25**, 725 (1929).

$$\begin{aligned} \nu_0^i - \nu_0 = \Delta\nu_0 = & (\rho - 1)(\omega_e'u' - \omega_e''u'') \\ & - (\rho^2 - 1)(\omega_e'x_e'u'^2 - \omega_e''x_e''u''^2) \\ & + (\rho^3 - 1)(\omega_e'y_e'u'^3 - \omega_e''y_e''u''^3) + \dots \end{aligned} \quad (10)$$

Eq. (10) can be used for calculating the direction and magnitude of the isotope shift when the data are sufficient to give an analytic function representing the bands. This is more general than Loomis's Eq. (7)⁸ and is in terms of half integral quantum numbers.

As shown by Birge, an approximate equation can be written for Eq. (9):

$$G_u^i - G_u = (\rho - 1)\omega_u u. \quad (11)$$

This gives, on transition,

$$\Delta\nu_0 = (\rho - 1)(\omega_u'u' - \omega_u''u''). \quad (12)$$

The advantage of Eq. (12) is that it can be used independently of any functional form of G_u . It is necessary only to know the values of ω_u for the band whose isotope shift is to be calculated. The value of ω_u may be read directly from the $\omega_u : u$ curve, or interpolated linearly between $\omega_{u+1/2}$ and $\omega_{u-1/2}$, which are obtained directly from the spectrum.

This theory shows that the isotope effect is zero at the true origin of the band system. It also shows that the isotope shift does not increase uniformly as u increases. For, by differentiating Eq. (9) and equating the result to 0, a maximum value of the shift for a certain value $u = u_c$ is obtained. In case the $\omega_u : u$ curve is linear, u_c is approximately $1/2u_0$. The theory shows further that the apparent heats of dissociation D_e and D_e^i are equal. Geometrically, the $\omega_u : u$ curves for the main molecule and the isotope molecule cross each other at $u = u_c$, and the area under each is the same since $u_0/u_0^i = \rho$ and $\omega_e^i/\omega_e = \rho$. But the true heats of dissociation D_0 and D_0^i are not the same. The theory has been verified by Patkowski and Curtis⁷ by application to the bands of ICl, and by Birge⁴ to ICl and Cl₂, both of which involve isotope effects in the region of relatively high quantum numbers.

ISOTOPE EFFECT IN AgCl

The $\omega_u : u$ curves for the four isotopic molecules Ag¹⁰⁷Cl³⁵, Ag¹⁰⁹Cl³⁵, Ag¹⁰⁷Cl³⁷, and Ag¹⁰⁹Cl³⁷ are shown in Fig. 3. The curves for the excited states of the two Ag isotope molecules are not shown, since they almost coincide with the other two curves. The curves A'' and B'' for the normal states of the first set of Cl isotope molecules are very nearly parallel and show no intersection. But this is to be expected, since the extrapolated value of u_0'' was 148, and therefore u_c is about 74. However, the extrapolated values of ω_e for these molecules are in the ratio $336/343.6 = 0.978$, in close agreement with the calculated value of $\rho = 0.9794$. Also, for the strong pair of silver isotope bands, curves C'' and A'' , the ratio $\omega_e^i/\omega_e = 342.4/343.6 = 0.997$ in close agreement with $\rho = 0.9977$. However, due to the slight uncertainty in determining the

⁸ Bull. Natl. Res. Council, No. 57 (1926) p. 262.

TABLE III. *Isotope shifts.*

(v', v'')	$\text{Ag}^{107}\text{Cl}^{37} - \text{Ag}^{107}\text{Cl}^{35}$				$\text{Ag}^{109}\text{Cl}^{37} - \text{Ag}^{109}\text{Cl}^{35}$	
	$\rho - 1 = -0.020577$				$\rho - 1 = -0.020672$	
	$\Delta\nu$ obs	I $\Delta\nu$ calc	II $\Delta\nu$ calc	III $\Delta\nu$ calc	$\Delta\nu$ obs	$\Delta\nu$ calc
(2, 0)	—	-9.28	-8.27			
(3, 1)	-6.5	-6.42	-6.39	-8.08		
(4, 2)	-3.0	-2.72	-2.94	-5.77		
(1, 0)	-4.6	-4.56	-4.57	-4.81		
(2, 1)	—	-2.31	-2.30	-3.10		
(3, 2)	—	+0.45	+0.49	-1.12		
(0, 0)	—	+0.70	+0.69	+0.67		
(1, 1)	+2.5	+2.41	+2.39	+2.13		
(2, 2)	+3.5	+4.57	+4.58	+3.89		
(0, 1)	+7.2	+7.67	+7.67	+7.70		
(1, 2)	+8.6	+9.29	+9.24	+9.14		
(2, 3)	+9.5	11.35	11.37	10.77		
(3, 4)	12.8	13.93	13.92	12.67		
(0, 2)	14.3	15.84	14.54	14.68	14.4	14.56
(1, 3)	15.9	16.08	16.08	16.09	15.8	16.08
(2, 4)	17.7	18.04	18.06	17.69	18.0	18.03
(3, 5)	20.3	20.51	20.56	19.51	20.4	20.52
(4, 6)	23.4	23.86	23.63	21.63	23.3	23.86
(1, 4)	22.0	22.77	22.76	22.94	22.6	22.78
(2, 5)	24.2	24.63	24.65	24.51	24.1	24.65
(3, 6)	26.7	27.03	27.04	26.30	26.9	27.04
(4, 7)	29.6	30.25	31.94	28.36	30.3	30.29
(2, 6)	—	31.14	31.15	31.28		
(3, 7)	—	33.42	33.47	33.03		

TABLE III (continued)

(v', v'')	$\text{Ag}^{109}\text{Cl}^{35} - \text{Ag}^{107}\text{Cl}^{35}$		$\text{Ag}^{109}\text{Cl}^{37} - \text{Ag}^{107}\text{Cl}^{37}$	
	$\rho - 1 = -0.002264$		$\rho - 1 = -0.002360$	
	$\Delta\nu$ obs	$\Delta\nu$ calc	$\Delta\nu$ obs	$\Delta\nu$ calc
(1, 2)	—	—	—	1.04
(2, 3)	—	—	1.2	1.27
(3, 4)	—	—	—	1.55
(0, 2)	1.7	1.60	1.8	1.63
(1, 3)	1.9	1.77	1.8	1.81
(2, 4)	1.9	1.99	2.2	2.02
(3, 5)	2.3	2.26	2.4	2.29
(4, 6)	2.6	2.62	2.6	2.66
(1, 4)	2.5	2.50	3.0	2.56
(2, 5)	2.7	2.71	2.5	2.76
(3, 6)	3.0	2.97	3.1	3.03
(4, 7)	2.9	3.33	3.8	3.38
(2, 6)	3.3	3.43	—	3.49
(3, 7)	3.3	3.68	—	3.75
(4, 8)	3.8	3.95	—	4.09
(4, 9)	4.2	4.71	—	

proper slopes, it cannot be verified from the data that D_e is the same for all the molecules and D_0 different.

Curves A' and B' for the excited states of the first set of Cl isotope bands apparently show approach of intersection. The value of u_0' could not be accurately determined, but probably lies between 15 and 23. Hence the cross-over value u_r' is probably just outside the range of observation.

Table III contains the observed and calculated isotope shifts. Values of $\Delta\lambda$ were calculated from the mean of the observed displacements from the original measurements of the plates, and not the difference between the mean wave-lengths of Table I. The observed $\Delta\nu$ were calculated from these $\Delta\lambda$. The values of $\rho - 1$ are also recorded in this table for the four sets of isotope bands. The main molecule in each case is written in italics. For the first set of Cl isotope bands, the calculated values of $\Delta\nu_0$ were obtained in three ways for comparison: column I using the approximate Eq. (12), column II the analytic Eq. (10), and column III the old equation $\Delta\nu = (\rho - 1)\nu_u$ where ν_u is the difference between the wave-numbers of the head of the main molecule and ν_e , the origin of the band system. All three methods agree about equally well for most of the shifts. But Eqs. (10) and (12) are superior when high values of u' are involved. The old equation gives very poor agreement for bands having a high u' and low u'' . This is to be expected, since III should agree asymptotically with I and II for low quantum numbers, and the greatest departure of III should occur when u is relatively high, as it is here in the excited state. The observed values of u in the normal state are relatively low.

The shifts for the other sets of isotope bands were calculated by Eq. (12). The observed shifts for the Ag isotopes are somewhat erratic due to the smallness of separation of the heads and their lack of sharpness, as well as their faintness in some cases. The results here confirm the existence of two isotopes of silver, of relative mass 107 and 109.

PRODUCTS OF DISSOCIATION

It has been shown by Franck,⁹ Dymond,¹⁰ and others that when absorption of light by an "atom-molecule" results in dissociation by vibration from the excited state, at least one of the resulting atoms is excited. From a study of the $\omega_u : u$ curves in the normal state, Birge and Sponer¹¹ showed it quite probable that most molecules in dissociating by vibration from the normal state yield two normal atoms. The difference between the total energy (measured from the normal state) required to dissociate the molecule in the two cases should correspond to the amount of excitation of the resulting atoms. Hence, if a continuous spectrum exists which corresponds to the convergence limit of the $u'' = 0$ progression of the vibration bands, then by subtracting the lowest excitation energy in one of the resulting atoms from the long wave-length limit of this continuum, a value for the normal heat of dissociation D_0'' is obtained. For example, this was done by Dymond for I_2 .

⁹ J. Franck, *Trans. Far. Soc.* **22**, 536 (1925).

¹⁰ Dymond, *Zeits. f. Physik* **34**, 553 (1925).

¹¹ Birge and Sponer, see ref. 5.

Conversely, if it is possible from the data for a given molecule to determine the heats of dissociation in both the normal and excited states, it is sometimes possible to find the states of the atoms resulting by dissociation.

In their work on the silver halides, Franck and Kuhn¹ report a continuous spectrum for AgI overlapping the discontinuous bands, and showing a maximum at $\lambda 3170$. The long wave-length edge is variable with temperature and pressure. Assuming a normal silver atom and an excited (metastable) iodine atom formed by dissociation, and adding to this atomic energy the thermochemical value of D_0'' , they obtained an energy value agreeing approximately with the observed long wave-length limit at $\lambda 3740$. It appears to the writer that the use of the long wave-length limit of this continuum is in this case not at all reliable. Furthermore, the writer's conclusions as to the products of dissociation differ from Franck and Kuhn's. The use of the maximum at $\lambda 3170$, which is on the high frequency side of the bands, would give close agreement. The same criticism would apply to AgBr. No continuous spectrum appeared with AgCl.

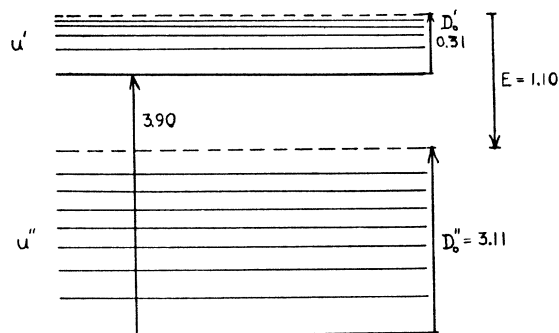


Fig. 4. Energy relations in AgCl.

Fig. 4 summarizes the results obtained in the present paper for AgCl. $D_0'' = 3.11 \pm 0.10$ volts, $D_0' = 0.31 \pm 0.02$ volt, and the energy corresponding to the (0, 0) band is 3.90 volts. This leaves 1.10 ± 0.12 volts as the electronic excitation of the atoms resulting by dissociation. In accounting for this energy, several possibilities must be examined. If the products are: (1) Ag^+ and Cl^- , the resultant energy would be the ionization potential of Ag minus the electron affinity of Cl, or $7.53 - 4.1 = 3.42$ volts. (2) Normal Ag and excited Cl; the separation ${}^2P_{1/2} - {}^2P_{3/2}$ in the normal state of Cl is 0.11 volt. This is the process which would be assumed consistent with Franck and Kuhn's conclusions. Other levels in the Cl atom may be excluded because of their high energy. (3) Excited Ag and normal Cl; this case was barred by Franck because of the large separation between the 2P and 2S levels of silver. (4) Both atoms excited.

The present results definitely exclude cases (1) and (2) even allowing a wide limit of error. However, (3) and (4) may be considered. Now in both Cu and Au there exist 2D states between the 2P and 2S states, due to terms based

on the d^9s configuration of the ion.¹² The lines of the Ag spectrum have not been completely classified, but since Ag stands between Cu and Au in the periodic table, it is a plausible assumption that these low-lying states exist also in Ag.¹³ If the silver halides dissociate into a normal halogen atom and a silver atom in this metastable $^2D(d^9s^2)$ state, then the electronic energy obtained as indicated in Fig. 4 should be *constant* for all three silver halides.

The writer has succeeded in assigning vibrational quantum numbers to Franck and Kuhn's data¹ for AgI and AgBr. This assignment is shown in

AgI														
$v'' \setminus v'$	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	×	×	×	×	×	×	×	×		×	×	×	×	×
1	×	×	×			×	×	×						
2	×													
3	×													
4	×													

AgBr														
$v'' \setminus v'$	0	1	2	3	4	5	6	7	8	9	10	11	12	13
0	×	×	×	×	×	×	×	×	×	×	×	×		
1			×		×	×	×	×	×					
2			×	×	×	×	×	×	×	×				
3														

Fig. 5. Assignment of vibrational quantum numbers to AgI and AgBr.

Fig. 5, which includes both absorption and fluorescence bands. Approximate equations representing the bands are as follows:

$$\begin{aligned} \text{AgI: } \nu &= 31153 + 127.5v' - 5.7v'^2 - 205.7v'' + 0.57v''^2, \\ \text{AgBr: } \nu &= 31421 + 179.4v' - 9.5v'^2 - 249.4v'' + 0.83v''^2. \end{aligned}$$

This gives for AgI, $\omega_0'' = 205.7 \text{ cm}^{-1}$ and $\omega_0''x'' = 0.57$, and for AgBr $\omega_0'' = 249.4$, $\omega_0''x'' = 0.83$. These agree with the values deduced by Birge from Franck and Kuhn's data, 205.8, 0.56, 247.2, and 0.81 respectively.¹⁴ On account of the uncertainty of the measurements, the $\omega_u: u$ curves are uncertain, and the heats of dissociation obtained by this data are not very accurate. But it is certain that the heats of dissociation in the excited states are very small and therefore a large error in determining them by extrapolation will not affect the results appreciably.

¹² Grotrian, Graphische Darstellung von Atomen . . . I, p. 73, II, p. 44, 51, A. G. Shensstone, Phys. Rev. **28**, 449 (1926) Cu.

¹³ But the d^9s configuration of Ag is expected to be more stable for Ag than for Cu or Au. See Hund's "Spectrallinien" p. 169-170; also R. Ruedy, Jour. de Phys. et le Radium **10**, 129 (1929); also Trans. Far. Soc. **25** (Dec. 1929) p. 752 (Bengtsson and Hulthén). For evidence of *instability* see J. Kaplan Zeits. f. Phys. **52**, 883 (1929).

¹⁴ Int. Crit. Tables, Vol. V, p. 411 (Birge's table).

As in Fig. 4 we may now calculate approximately the resulting electron excitation E of the dissociation products by the sum $\nu_0 + D_0' - D_0'' = E$, where ν_0 represents the energy corresponding to the (0, 0) band. For AgBr and AgI we will use the thermochemical values¹⁴ for D_0'' and the extrapolated values from the above analysis for D_0' .

$$\text{AgCl: } 3.90 + 0.31 - 3.11 = 1.10$$

$$\text{AgBr: } 3.88 + 0.11 - 2.6 = 1.39$$

$$\text{AgI: } 3.85 + 0.09 - 2.0 = 1.94$$

The resulting values of E are thus not constant. But if we now subtract from these values of E the ${}^2P_{1/2} - {}^2P_{3/2}$ separation in the normal states of the halogens, which are respectively 0.11, 0.46, 0.94 volt¹⁵ we obtain for E in the three cases 0.99, 0.93, 1.00 volt respectively, which is now very nearly constant. This indicates that the silver halides dissociate from the excited state into a silver atom in a ${}^2D(d^9s^2)$ state and a halogen atom in the ${}^2P_{3/2}$ state.

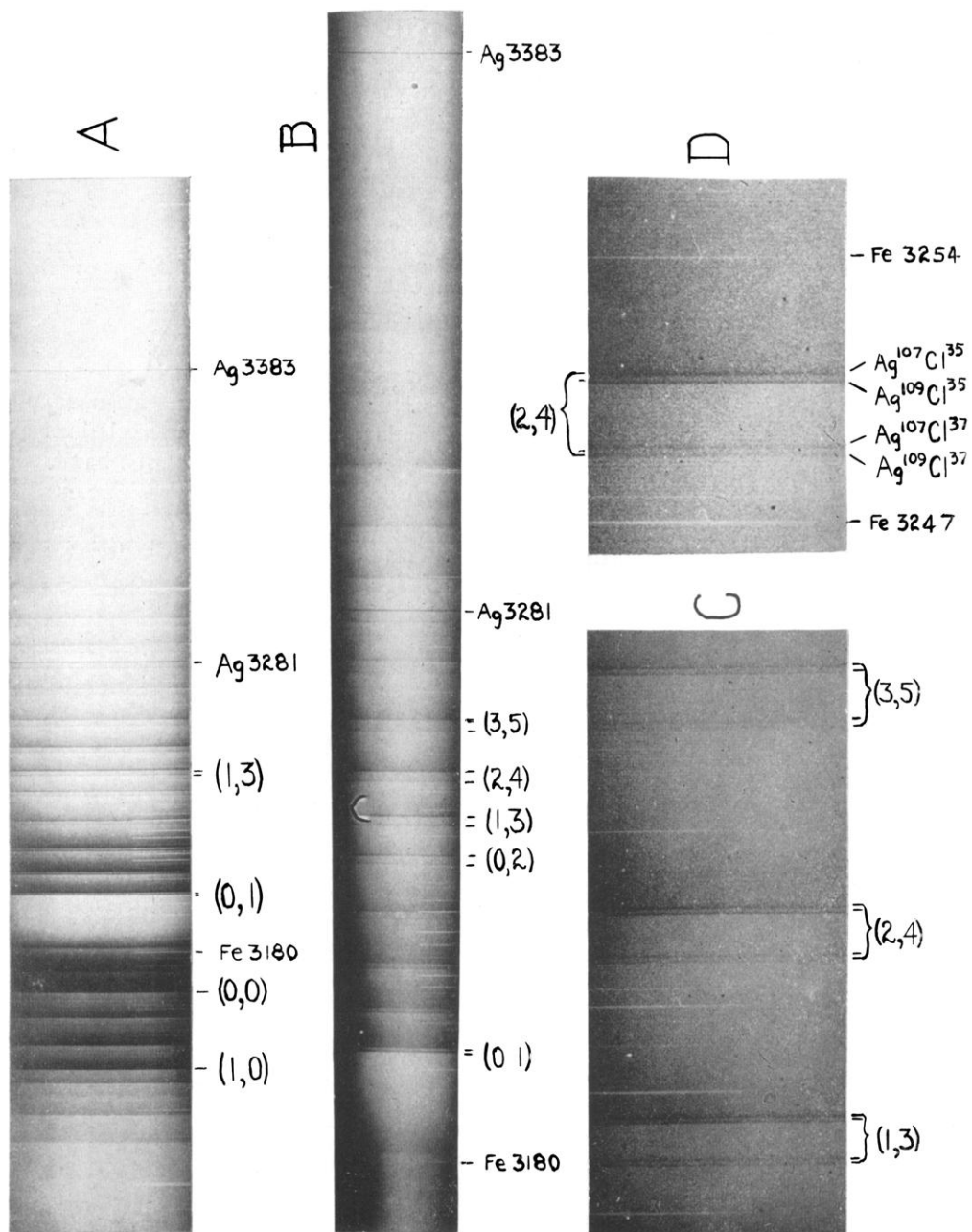
As in Cu and Au, combinations may occur in the silver atom between the 2P and these ${}^2D'$ terms. Assuming the ${}^2D'$ level to be 0.99 ± 0.1 volt, or $8000 \pm 800 \text{ cm}^{-1}$, above the normal 2S level, we would expect a line in the Ag spectrum at $4400 \pm 150 \text{ \AA}$ for the transition ${}^2P_{3/2} - {}^2D_{3/2}'$. There are several fairly strong unclassified lines in this region. Referring to Kayser's Handbuch Vol. VII, the two lines $\lambda 4888.3 (2u)$ and $\lambda 4677.9 (4u)$ have a wave-number separation 920 cm^{-1} , which agrees with the 2P doublet separation. They are the only lines found giving this difference. Hence it is possible that they correspond to transitions ${}^2P_{3/2} - {}^2D_{1/2}'$ and ${}^2P_{1/2} - {}^2D_{1/2}'$ in Ag. The next line of the same type as these two is $\lambda 4396.3 (2u)$. If this is the ${}^2P_{3/2} - {}^2D_{3/2}'$ line, this leaves 7731 cm^{-1} or 0.955 volt for the ${}^2D' - {}^2S$ separation. This is in close agreement with the above value $E = 0.99$ volt deduced from the band spectrum of AgCl. Extrapolations such as were made in obtaining this value should be done cautiously. But even allowing a wide limit of error, the conclusions seem to be unaffected.

The above agreement may indeed be accidental, and awaits further testing by the final analysis of the Ag spectrum,* and by more accurate work on the band spectra of AgI and AgBr. The latter will be carried out by the author in the near future.

In conclusion, the writer expresses much appreciation for the valuable suggestions and constant interest of Dr. F. A. Jenkins, under whom this work was begun. I also am greatly indebted to Professor R. T. Birge for use of his manuscript on the vibrational isotope effect. Suggestions and interest of Dr. F. W. Loomis, and Dr. G. Breit were also helpful.

¹⁵ L. A. Turner, Phys. Rev. **27**, 397 (1926).

* Dr. A. G. Shenstone has kindly informed me that his recent work on the Ag spectrum predicts these ${}^2D(d^9s^2)$ terms to be near 30000 cm^{-1} , close to the 2P terms, with a doublet separation of about 5000 cm^{-1} . He believes that the lines mentioned above are due to the terms ${}^4P^{\circ}D^{\circ}F^{\circ}(d^9sp)$ combining with ${}^4D(d^9s, s)$, though he has not as yet been able to identify them. If this is correct, the value of E obtained by the writer remains unexplained.



SILVER CHLORIDE ABSORPTION

Fig. 1.